X -> 1-10 D2
Y -> 11.13

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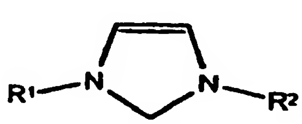
(54) Title: IMIDAZOLE CARBENES



(I)

(57) Abstract: A process for the preparation of imidazolium carbenes of formula (I) wherein R_1 and R_2 which can be the same or different, are hydrogen or linear or branched hydrocarbyl groups comprising heating an imidazolium halide with a strong base under reduced pressure and separating the resultant products is described. Also described is a process for the preparation of salts of these imidazolium carbenes, and their use as ionic liquids.

Imidazole Carbenes

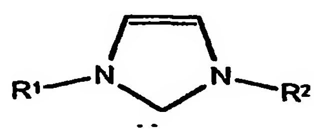
This invention relates to a process for the synthesis of imidazole carbenes and the use thereof for the synthesis of ionic liquids.

Carbenes are generally organic molecules which have a lone pair of electrons on a carbon atom and which in turn renders them highly reactive. As a result, carbenes are highly reactive intermediates in the synthesis of chemical compounds. Carbenes, due to their highly reactive nature, are generally only isolatable in the form of eg metal carbenoid species.

Numerous methods for the generation of imidazole carbenes have been reported. Starting from an imidazolium halide, the use of systems such as sodium hydride in ammonia or dimethyl sulfoxide (DMSO), sodium in ammonia, alkali metals in tetrahydrofuran (THF), metal *t*-butoxides in THF or DMSO, *etc*. These suffer from the disadvantage that very dry conditions and reagents have to be used, difficult separations under strictly anhydrous conditions are involved, and the reagents used can be expensive and inconvenient.

We have developed a simple procedure for the generation of the imidazolium carbene in 90-95% yield from an imidazolium chloride: this does not require solvents, filtrations, or lead to the production of noxious waste products.

According to the first aspect of the present invention, there is provided a process for the preparation of imidazolium carbenes of formula (I),



(I)

wherein R_1 and R_2, which can be the same or different, are hydrogen or linear or branched hydrocarbyl groups,

comprising heating an imidazolium halide with a strong base under reduced pressure and separating the resultant products.

The process is preferably carried out under vacuum. The resultant products can be separated using any known separation techniques such as distillation.

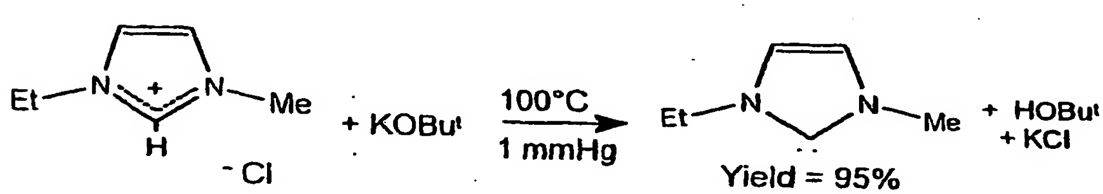
The imidazolium halide may suitably be a chloride, bromide or an iodide and is preferably a chloride. R_1 and R_2 are suitably alkyl, alkaryl, aryl or aralkyl groups, more preferably alkyl groups. These hydrocarbyl groups suitably have from 1-20 carbon atoms, preferably from 1-8 carbon atoms. Specifically these substituents may be methyl or ethyl groups.

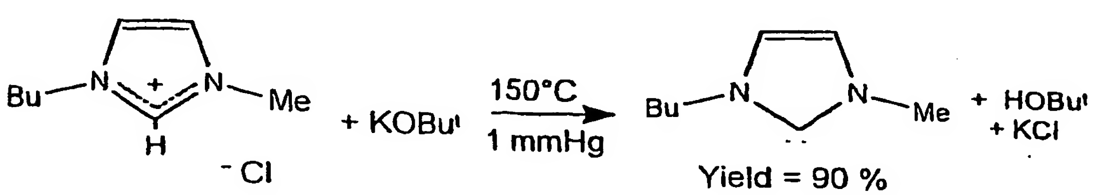
The strong base heated with the imidazolium halide may be any of the conventionally known strong bases such as eg alkali metal alkoxides, sodium hydride, sodium amide ($NaNH_2$) and the like. The strong base is suitably an alkali metal alkoxide in which the alkoxide group has 1-4 carbon atoms and may be a straight or branched chain. Specific examples of these are the methoxide, the ethoxide, the propoxide and the butoxide, especially the tertiary butoxide. Of the alkali metals in the alkoxide, potassium is preferred.

In one embodiment of the present invention, the process involves the distillation under vacuum of the carbene from a mixture of an imidazolium chloride and a commercially available metal alkoxide such as eg potassium *t*-butoxide. The commercial metal alkoxide need not be further purified before use. The by-products of this reaction, where an imidazolium chloride is heated with potassium *t*-butoxide, are potassium chloride and *t*-butanol (which can be recycled). The method is straightforward, relatively cheap, and does not involve the production of noxious waste products.

Two examples of the reaction are shown below in which the substituents on the imidazolium groups are represented by the following abbreviations:

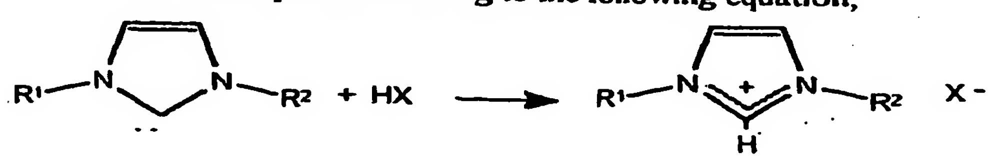
Et	-	Ethyl
Bu	-	Butyl
Me	-	Methyl
Bu^t	-	Tertiary butyl
$KOBu^t$ -	Potassium tertiary butoxide	
$HOBu^t$ -	Tertiary butanol	





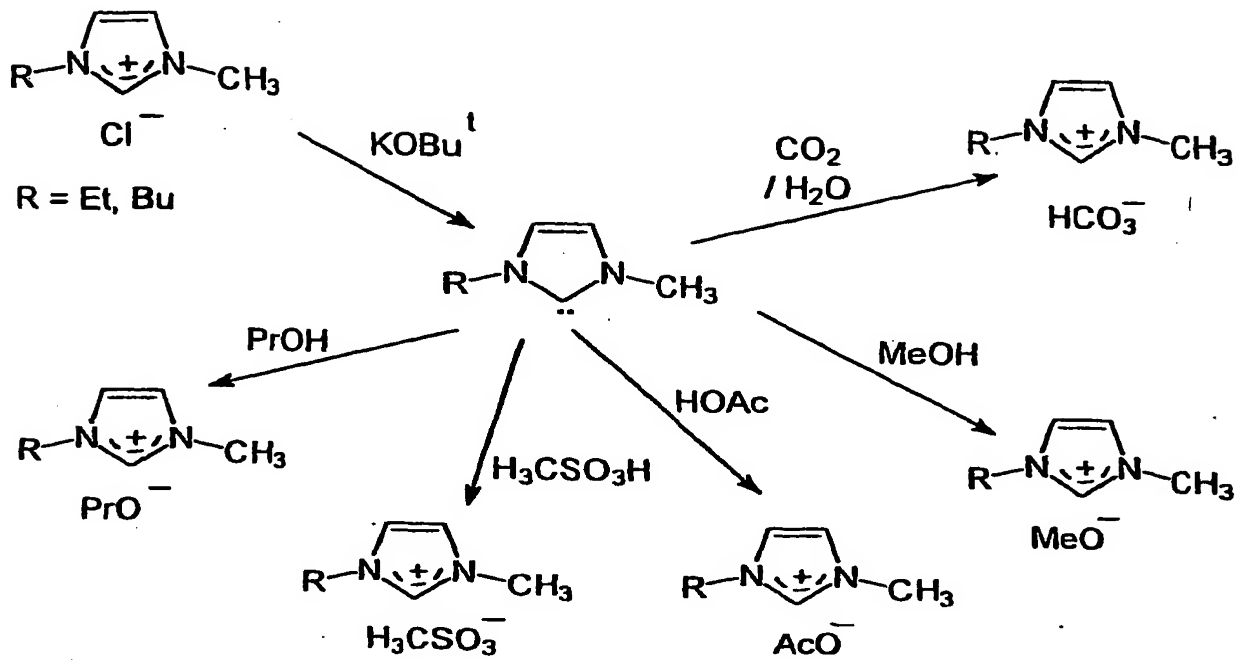
The two carbenes shown, which fume in moist air, are both colourless oils with a characteristic smell (freshly mown grass), of boiling point 90°C and 130°C at about 130 Pa (1 mm Hg) pressure, respectively. They appear to be thermally stable up to 200°C for short periods of time, and stable at room temperature for several days (the mode of decomposition appears to be water-promoted disproportionation to a 2H-imidazoline and an oxidised species). However, they are extremely hygroscopic, reacting with moisture in the air to form the corresponding imidazolium hydroxide, itself being a novel ionic liquid. Consequently, they must be handled under dinitrogen or in an inert atmosphere glove box. The reaction of forming carbene itself is carried out in the substantial absence of any solvents, However, once produced, to facilitate handling of the carbenes, it may be dissolved in solvents. Suitable solvents for the dissolution of carbenes are limited, but aromatic, aliphatic (alkanes) and ether solvents appear to be appropriate. Halogenated and ketonic solvents must not be used, especially carbon tetrachloride, chloroform and primary alkyl halides, owing to a rapid exothermic transformation.

These carbenes can be used for conversion thereof to the corresponding imidazolium salts by a simple reaction with the acid form of the required anion. This reaction takes place according to the following equation;



wherein R^1 and R^2 are as hereinbefore defined.

Thus, the present process can be used to generate imidazolium salts with a variety of anions such as those graphically represented in the equation below:



As can be seen from the above, the acid form of the anion can be any one of a vast variety of compounds including *inter alia* alcohols such as eg methanol or propanol, and acids such as eg carbonic acid, acetic acid or alkyl sulfonic acid

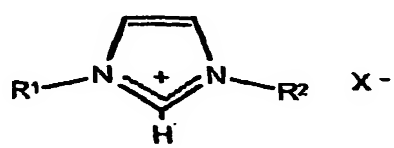
Imidazolium salts of this type are essential components of many ionic liquids which are used as catalysts or solvents for catalysts in chemical reactions such as eg dimerisation, oligomerisation and polymerisation of olefins. Ionic liquids are primarily salts or mixtures of salts which melt below, at or above room temperature. Such salt mixtures include (alkyl) aluminium halides in combination with one or more of imidazolium halides, the latter being preferably substituted eg by alkyl groups. Examples of the substituted derivatives of the latter include one or more of 1-methyl-3-ethylimidazolium halide, 1-methyl-3-butylimidazolium halide, 1-ethyl-3-butylimidazolium halide and the like. These ionic liquids consist of a mixture where the mole ratio of the (alkyl) aluminium halide to the imidazolium halide is usually > 1.0 but may be 1.0 or < 1.0. Ionic liquids may also be simple binary salts, such as 1-methyl-3-butylimidazolium hexafluorophosphate, 1-methyl-3-ethylimidazolium acetate and 1-methyl-3-butylimidazolium nitrate.

The advantage of making the imidazolium salts by the present process, ie by reaction of two neutral molecules, is that it generates ionic liquids which are not contaminated by unwanted halide ions or metal ions. In addition to providing a novel and convenient route to known ionic liquids, it also permits the generation of

novel ionic liquids, such as 1-methyl-3-alkylimidazolium alkoxides, 1-methyl-3-alkylimidazolium hydrogencarbonates and the corresponding imidazolium hydroxide which were hitherto unknown.

Thus according to a second aspect of the present invention, there is provided an imidazolium carbene of formula (I) as hereinbefore defined whenever prepared by the present invention.

According to a third aspect of the present invention, there is provided preparation of imidazolium salts of formula (II)



(II)

wherein R_1 and R_2, which can be the same or different, are hydrogen or linear or branched hydrocarbyl groups and X^- is a cation, comprising the reaction of an imidazolium carbene of formula (I) as hereinbefore defined with an acid or alcohol.

According to a fourth aspect of the present invention, there is provided an imidazolium salt of formula (II) as hereinbefore defined whenever prepared by the present invention.

According to a fifth aspect of the present invention, there is provided use of an imidazolium salt of formula (II) as hereinbefore defined as an ionic liquid.

The present invention is further illustrated with reference to the following Examples:

Examples:

1. **Preparation of Carbenes**

1.1 **1-Ethyl-3-methylimidazol-2-ylidine**

All manipulations were performed under a stream of dry dinitrogen or in a glove box. In a round-bottomed flask (50 cm^3), 1-ethyl-3-methyl imidazolium chloride (8.7 g, 50 mmol) and a commercial sample of potassium t-butoxide (7.7 g, 75 mmol, unpurified, 95% ex Aldrich) were heated in a Kugelrohr apparatus at 125°C at about 130 Pa (1 mm Hg) pressure for 1 h. A colourless oil was collected and transferred to a clean round-bottomed flask (50 cm^3). This was redistilled on the Kugelrohr apparatus to give 5.3 g of a colourless oil. NMR analysis showed this oil to be 1-ethyl-3-methylimidazol-2-ylidine (95 % yield). The product has a tendency to rapidly turn orange on contact with the air. The carbene produced by this Example was characterised using ^1H and ^{13}C NMR spectroscopy and the following peaks were identified:

^1H NMR	7.21	1H	singlet	^{13}C NMR	208.5	C
	7.08	1H	singlet		117.5	CH
	4.03	2H	quartet		116.2	CH
	3.73	3H	singlet		42.5	CH_2
	1.38	3H	triplet		34.7	CH_3
					14.6	CH_3

1.2 **1-Butyl-3-methylimidazol-2-ylidine**

The same procedure as in Section 1.2 above was used for making the analogous butyl carbene except that the reaction temperature and distillation temperature were slightly (*ca.* 30°C higher)

The carbene produced by this Examples was characterised using ^1H and ^{13}C NMR spectroscopy and the following peaks were identified:

^{1}H NMR	7.16	1H	singlet	^{13}C NMR	210.2	C
	7.02	1H	singlet		117.5	CH
	4.02	2H	quartet		116.7	CH
	3.68	3H	singlet		47.4	CH_2
	1.78	2H	pentet		34.6	CH_3
	1.38	2H	hextet		31.3	CH_2
	0.90	3H	triplet		17.1	CH_2
					10.9	CH_3

2. **Preparation of Imidazolium Salts:**

The method depends upon the careful mixing of a stoichiometric amount of carbene with an acid or alcohol, or, alternatively, excess acid, if the excess acid is readily separable (eg carbonic acid).

2.1 1-Butyl-3-methylimidazolium hydrogencarbonate:

A mixture of 1-butyl-3-methylimidazolium chloride (4.37g, 25 mmol) and potassium t-butoxide (3.95g, 35 mmol) was placed in a 50 cm^3 round bottomed flask in a glove box. The flask was transferred to a Kugelrohr apparatus and the mixture was heated at 150°C, at about 130 Pa (1 mm Hg) pressure. A colourless oil (1-butyl-3-methylimidazol-2-ylidine) was collected. The reaction was adjudged to be complete after 30 minutes and the oil was immediately poured into a 500 cm^3 round bottom flask containing de-ionised water (100 cm^3) and dry ice (*ca.* 10g). The flask was agitated until the dry ice had evaporated and the water was evaporated on a rotary evaporator. Toluene (3 x 50 cm^3) was added to the flask and removed on a rotary evaporator (this procedure was used to azeotropically remove water from the ionic liquid) and finally, the resultant viscous brown oil was heated to 50°C at 133.4 Pa (1 mm Hg) for 2 hours. Weight of product = 3.51g, yield = 70%. The same NMR spectroscopy as used previously to characterise the carbene was used to characterise the imidazolium salts. The results were as follows:

^{1}H NMR	8.85	1H	singlet	^{13}C NMR	159.0	C (HCO_3^-)
	7.61	1H	singlet		135.7	CH
	7.57	1H	singlet		122.0	CH
	4.99		singlet (HOD)		120.6	CH
	4.31	2H	triplet		47.7	CH_2
	4.02	3H	singlet		34.1	CH_3
	1.95	2H	hextet		29.7	CH_2
	1.42	2H	pentet		17.2	CH_2

	1.03	3H	triplet	11.2	CH_3

Solvent = D_2O

IR (NaCl plate): $\nu = 1666\ cm^{-1}$ C=O

$\nu = 3600\text{-}2350\ cm^{-1}$ O-H

Empirical solubilities:

Soluble:	water, methanol, ethanol
Partially soluble:	acetone
Insoluble:	ethyl acetate, diethyl ether

2.2 <u>1-Ethyl-3-methylimidazolium methoxide:</u>

A mixture of 1-ethyl-3-methyl imidazolium chloride (3.66g, 25 mmol) and potassium t-butoxide (3.96g, 35 mmol) was placed in a 50 cm^3 round bottomed flask in a glove box. The flask was transferred to a Kugelrohr apparatus and the mixture was heated at 140°C, at about 130 Pa (1 mm Hg) pressure. A colourless oil (1-ethyl-3-methylimidazol-2-ylidine) was collected. The reaction was adjudged to be complete after 30 minutes and the apparatus was repressurised with dry nitrogen. Anhydrous methanol (1.0 cm^3, 27 mmol) was added to the carbene by syringe. Excess methanol was removed by reconnecting to the vacuum line (1 mm Hg) and rotating the reaction vessel for 1 hour. The NMR spectra were recorded neat, using an acetone-d^6 external lock. Yield estimated at 85-90% (based on NMR)

^1H NMR	8.99	1H	singlet (broad) ^{13}C NMR	190.2	CH	(broad)
	7.56	1H	singlet	118.4	CH	
	7.45	1H	singlet	116.4	CH	
	4.38	2H	quartet	45.1	CH_2	
	4.02	3H	singlet	42.3	CH_3	
	3.66	3H	singlet	34.0	CH_3	
	1.63	3H	triplet	14.0	CH_3	

Note: The product is extremely hygroscopic and decomposes slowly at room temperature. This decomposition appears to be water catalysed.

2.3 <u>1-Butyl-3-methylimidazolium propoxide:</u>

1-Butyl-3-methylimidazol-2-ylidine (2.00 g, 16.1 mmol) was prepared as in Section 2.1 above. This was cautiously added to n-propanol (0.97g, 16.1 mmol) by pipette in a glove box. The NMR spectra were recorded neat, using an acetone-d^6 external lock. Yield estimated at 95% (based on NMR)

^{1}H NMR	8.92	1H	singlet (broad)	^{13}C NMR	190.1	CH	(broad)
	7.46	1H	singlet		118.2	CH	
	7.41	1H	singlet		117.3	CH	
	4.33	2H	triplet		59.8	CH_2	
	4.02	3H	singlet		47.2	CH_2	
	3.86	2H	triplet		34.0	CH_3	
	2.10	2H	pentet		30.9	CH_3	
	1.86	2H	hexet		29.0	CH_2	
	1.60	2H	hexet		24.3	CH_2	
	1.20	3H	triplet		10.8	CH_3	
	1.19	3H	triplet		8.0	CH_3	

Note: The product is extremely hygroscopic and decomposes very slowly at room temperature. This decomposition appears to be water catalysed. It appears to be significantly more stable than 1-ethyl-3-methylimidazolium methoxide.

2.4 <u>1-Butyl-3-methylimidazolium acetate:</u>

1-Butyl-3-methylimidazol-2-ylidine (2.00 g, 16.1 mmol) was prepared as in Section 2.1 above. This was cautiously added to glacial acetic acid (0.97g, 16.1 mmol) by pipette in a glove box over a 15 minute period. The NMR spectra were recorded neat, using an acetone-d^{6} external lock. Yield estimated at 95% (based on NMR).

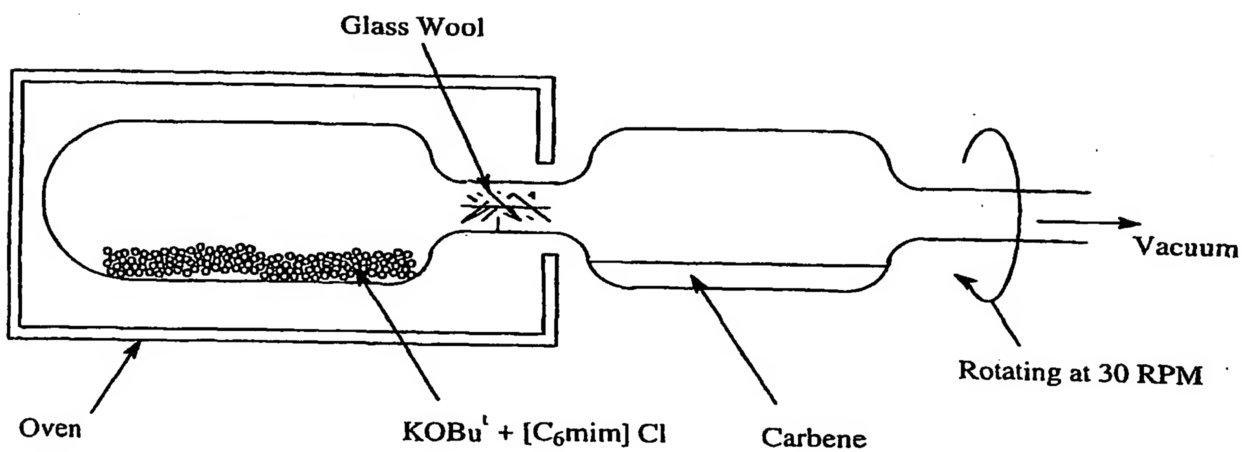
^{1}H NMR	10.61	1H	singlet	^{13}C NMR	172.1	C
	8.45	1H	singlet		136.3	CH
	8.32	1H	singlet		121.6	CH
	4.31	2H	triplet		120.5	CH
	4.02	3H	singlet		46.0	CH_2
	1.72	2H	pentet		32.8	CH_3
	1.70	3H	singet		29.6	CH_2
	1.15	2H	hexet		28.6	CH_3
	0.72	3H	triplet		22.2	CH_2
					10.4	CH_3

The following are further non-limiting examples;

1-hexyl-3-methylimidazolylidine.

1-hexyl-3-methylimidazolium chloride (10.0 g) was placed in a 100 cm^3 Kugelrohr flask and connected to a Kugelrohr apparatus (Fig. 1,2). This was heated at 100 °C for 1 hour at 1 mmHg pressure, then cooled to room temperature. The flask was transferred to a dry glove box and potassium *tert*-butoxide (10.0 g) was added to the 1-hexyl-3-methylimidazolium chloride. The apparatus was reassembled and heated at 160 °C for 2 hours. During this period, 1-hexyl-3-methylimidazolylidine distilled into the receiving flask and the *tert*-butanol condensed into a liquid nitrogen trap connected to the vacuum pump. The orange coloured 1-hexyl-3-methylimidazolylidine was analysed by ^1H and ^{13}C NMR spectroscopy. The crude product was redistilled in the Kugelrohr apparatus (bp = 160°C at 1 mmHg) to give an extremely moisture sensitive colorless oil (6.5 g, 79 %); δH (300 MHz, neat, external TMS reference) 6.97 (1H, s), 6.92 (1H, s), 3.94 (2H, q, J = 7.3 Hz), 3.62 (3H, s), 1.72 (2H, m), 1.26 (6H, m), 0.85 (3H, t, J = 7.3 Hz); ^{13}C NMR δC (75 MHz, neat, external TMS reference) 209.6 (C), 119.6 (CH), 118.5 (CH), 49.9 (CH_2), 35.7 (CH_3), 31.5 (CH_2), 31.3 (CH_2), 31.1 (CH_2), 22.1 (CH_2), 13.4 (CH_3).

Figure 1: the apparatus for the synthesis of imidazolium carbenes.



1-Hexyl-3-methylimidazolium hydrogen carbonate
Solid carbon dioxide (dry ice) (*ca.* 25 g) was added to distilled water (100 g), with stirring from a magnetic stirring flea in a 500 cm^3 beaker, in a fume hood. 1-hexyl-3-methylimidazolylidine (6.0 g, 36.1 mmol) was added to the water and carbon dioxide mixture. The mixture was allowed to warm to room temperature, and was washed with dichloromethane (3 x 25 cm^3). The water was evaporated on a rotary evaporator (making sure the temperature did not exceed 60 °C) and the 1-hexyl-3-methylimidazolium hydrogen carbonate was dried under vacuum (1 mmHg) for 4 hours at 60 °C. This gave 7.8 g (94 %) of a straw coloured viscous liquid. δH (300 MHz, D_2O, TMS reference) 8.28 (1H, s, D_2O exchangable) 7.43 (1H, s), 7.33 (1H, s), 4.78 (1H, s), 4.04 (2H, q, J = 7.3 Hz), 3.77 (3H, s), 1.73 (2H, m), 1.32 (6H, m), 0.71 (3H, t, J = 7.3 Hz); ^{13}C NMR δC (75 MHz, D_2O, TMS reference) 161.3 (C), 135.8 (CH, D_2O exchangeable), 123.8 (CH), 122.5 (CH), 49.8 (CH_2), 35.9 (CH_3), 30.6 (CH_2), 29.5 (CH_2), 25.3 (CH_2), 22.1 (CH_2), 13.6 (CH_3).

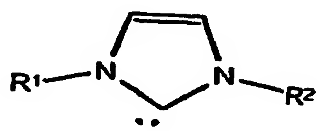
This salt could be converted to other 1-hexyl-3-methylimidazolium salts (or ionic liquids) by reaction with the acid form of the desired anion in water, followed by evaporation of the water.

1-Octyl-3-methylimidazolylidine.
1-Octyl-3-methylimidazolium chloride (5.0 g, 21.7 mmol) was placed in a 50 cm^3 Kugelrohr flask and connected to a Kugelrohr apparatus (Fig 1). This was heated at 100 °C for 1 hour at 1 mmHg pressure, then cooled to room temperature. The flask was transferred to a dry glove box and potassium *tert*-butoxide (5.0 g, excess) was added to the 1-octyl-3-methylimidazolium chloride. The apparatus was reassembled and heated at 200 °C for 1 hour. During this period, 1-octyl-3-methylimidazolylidine distilled into the receiving flask and the *tert*-butanol condensed into a liquid nitrogen trap connected to the vacuum pump. The crude product was redistilled in the Kugelrohr apparatus (bp = 190-200 °C at 1 mmHg) to give an extremely moisture sensitive oil (2.87 g, 68 %). The yellow coloured 1-octyl-3-methylimidazolylidine solidified on standing was immediately used in further reactions.

1-Octyl-3-methylimidazolium acetate
1-Octyl-3-methylimidazol-2-ylidine (2.00 g, 16.1 mmol) prepared above, was cautiously added to glacial acetic acid (0.97g, 16.1 mmol) by pipette in a glove box over a 15 minute period with stirring from a magnetic stirrer flea. The ionic liquid foumed was used unpurified. NMR data: δH (300 MHz, neat, external TMS reference) 10.61 (1H, s), 8.45 (1H, s), 8.32 (1H, s), 4.31 (3H, t), 4.02, (3H, s), 1.72 (2H, m), 1.70 (2H, s), 1.15 (10H, m), 0.72 (3H, t, J = 7.2 Hz); ^{13}C NMR δC (75 MHz, neat, external TMS reference) 172.1 (C), 136.3 (CH), 121.6 (CH), 120.5 (CH), 46.0 (CH_2), 32.8 (CH_3), 29.6 (5 x CH_2), 28.6 (CH_3), 22.2 (CH_2), 10.4 (CH_2).

Claims

1. A process for the preparation of imidazolium carbenes of formula (I),



(I)

wherein R_1 and R_2, which can be the same or different, are hydrogen or linear or branched hydrocarbyl groups, comprising heating an imidazolium halide with a strong base under reduced pressure and separating the resultant products.

2. A process according to claim 1 wherein the separation involves distillation with the imidazolium carbene being present in the distillate.

3. A process according to claim 1 or Claim 2 wherein the imidazolium halide is an imidazolium chloride.

4. A process according to any one of the preceding Claims wherein R_1 and/or R_2 are C_{1-20} alkyl, alkaryl, aryl or alalkyl groups.

5. A process according to Claim 4 wherein R_1 and/or R_2 are C_{1-8} alkyl groups.

6. A process according to Claim 5 wherein R_1 and/or R_2 are methyl or ethyl groups.

7. A process according to any one of the preceding claims wherein the strong base is a sodium hydride or sodium amide.

8. A process according to any one of Claims 1-6 wherein the strong base is an alkali metal alkoxide.

9. A process according to Claim 8 wherein the alkoxide is a C_{1-4} alkoxide.

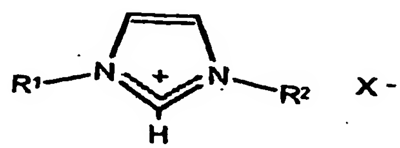
10. A process according to Claim 9 wherein the alkoxide is tertiary butoxide.

11. A process according to any one of Claims 8-10 wherein the alkali metal is potassium.

12. A process according to any one of Claims 1 to 11 carried out wholly or substantially in the absence of a solvent.

13. An imidazolium carbene whenever prepared by a process according to any one of Claims 1 to 12.

14. A process for the preparation of an imidazolium salt of formula (II)



(II)

wherein R_1 and R_2, which can be the same or different, are hydrogen or linear or branched hydrocarbyl groups and X^- is a cation, in which an imidazolium carbene of formula (I) as defined in Claim 1 is reacted with an acid or alcohol.

15. A process according to Claim 14 wherein R_1 and R_2 are as defined in any one of Claims 4-6.

16. An imidazolium salt wherever prepared by a process according to any one of Claims 14 or 15.

17. Use of an imidazolium salt as defined in Claim 14 as an ionic liquid.

18. Use of animidazolium salt according to Claim 17 additionally comprising one or more aluminium halides or alkyl aluminium halides.

19. Use of an imidazolium salt according to Claim 17 or Claim 18 as a catalyst.

20. Use of an imidazolium salt according to Claim 17 or Claim 18 as a solvent.

21. Use of an imidazolium salt according to any one of Claims 17-20 in the catalysis of olefin dimerisation, oligomerisation or polymerisation.

22. A 1-methyl-3-alkylimidazolium alkoxide.

23. A 1-methyl-3-alkylimidazolium hydrogencarbonate.

24. A 1-methyl-3-alkylimidazolium hydroxide.

25. Use of a compound as defined in any one of Claims 22, 23 or 24 as an ionic liquid.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/GB 01/01487

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C07D233/06 C07D233/10

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C07D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

CHEM ABS Data, EPO-Internal, WPI Data, PAJ, BEILSTEIN Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
E	WO 01 40146 A (QUEEN'S UNIVERSITY OF BELFAST, UK) 7 June 2001 (2001-06-07) the whole document ---	1-25
P,X	CARMICHAEL, ADRIAN J. ET AL: "Molecular layering and local order in thin films of 1-alkyl-3- methylimidazolium ionic liquids using X-ray reflectivity" MOL. PHYS. (2001), 99(10), 795-800 , XP001008042 the whole document ---	16,17, 19-21

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"O" document referring to an oral disclosure, use, exhibition or other means

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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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Date of the actual completion of the international search	Date of mailing of the international search report
19 July 2001	31/07/2001

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Scruton-Evans, I

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A	WO 98 27064 A (GOERLICH JENS ROBERT ;ARDUENGO ANTHONY JOSEPH III (US); DU PONT (U) 25 June 1998 (1998-06-25) the whole document	1-25
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PC,/GB 01/01487

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